SULPHITE WASTE LIQUOR

AND

ITS POSSIBLE UTILIZATION

DISSERTATION

Submitted in Partial Fulfillment of the Requirement
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science, Columbia
University, in the City of
New York

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New York City
1922

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ACKNOWLEDGMENT

The author wishes to express to Professor Ralph H. McKee his most sincere thanks for the direction and suggestion of this work and for the many helpful suggestions made and encouragement offered during its prosecution.

Chemical Engineering Department
Columbia University

Dedicated
to the late

Samuel Willard Bridgham, '67 Mines

Sulphur in Sulphite Waste Liquor

The sulphite process for the production of pulp, involving as it
does the cooking of wood with calcium bisulphite solution con-
taining an excess of sulphur dioxide, may be regarded as a chemical
process having for its object the dissolving out of all of the con-
stituents of the wood except the cellulose. A part of the wood is
soluble in water[1], [2], without any noticeable chemical reaction. Ac-
cording to Klason,[2] this amounts to about twelve per cent of the
weight of spruce wood. The reactions, whatever they are, result
in the addition of sulphur to the organic matter that goes into
solution. We have investigated the form of combination of the
sulphur in the liquor and from our results we have concluded that
there are at least three distinct forms in which the sulphur is
present in organic combination, in addition to that present as free
SO_2, bisulphite, and normal sulphite.

It is commonly supposed that the waste liquor contains at least
two sulphonic acids of lignin. Klason[2], [3] has separated two "lignin-
sulphonic acid" salts from waste liquor, one by salting out with
calcium chloride and the other by treatment of the residual solution
from the salting out operation with naphthylamine hydrochloride.
He considers that the original lignin may be regarded as being
composed of 63 per cent of one and of 37 per cent of the other[4], [5].
It is possible that there may be several lignins, such as the "proto-,
hemi-, and ortholignins," suggested by König and Rump.[6] There
may be several compounds in the liquor all derived from the same
basic compound or compounds by some slight chemical change,
such as a mild oxidation, or the splitting out of sulphur dioxide
from the molecule, etc.

Indeed, despite the common statement that the principal con-
stituents of the liquor are ligninsulphonic acids or their salts, abso-
lute proof that some of the sulphur is present in the form of a
sulphonic acid grouping is lacking. Hönig and Fuchs[7] found that
by alkali fusion of "barium ligninsulphonate" at 300° C. they could
split off 90 per cent of the sulphur, and could recover 15 to 19 per
cent of the organic matter as catechol and protocatechuic acid. In
the light of these results they maintain that the nucleus of the
lignin is similar to that of protocatechuic acid. They also con-

[1]Shorger, A. W. J. Ind. Eng. Chem. 9, 560 (1917).
[2]Klason, P. Beitrage zur Kenntniss der Chemischen Zusammensetzung der
Fichtenholzes. Berlin, 1911.
[3]Klason, P. Arkiv. Kemi. Min. Geol., 6, No. 15, 1-21 (1917). C. A., 14,
2167.
[4]Klason, P. Ber. 53B, 1862 (1920); C. A. 15, 859.
[5]Klason, P. Ber. 53B, 1864 (1920); C. A. 15, 860.
[6]König, J. and Rump, E. Chemie und Struktur der Pflanzen-Zellmem-
bran. Berlin. 1914.
[7]Hönig, M. and Fuchs, W. Monatsh. 40, 341 (1919)

sider that these results prove that the sulphur is combined in the form of a sulphonic acid of an aromatic nucleus. However, this is not conclusive, as they have no proof that the hydroxyl groups are formed by alkali fusion in the same way that phenol is formed from benzenesulphonic acid by alkali fusion. The catechol and protocatechuic acid may be formed by a rearrangement during fusion. Cellulose on alkali fusion will give these substances. For example, Hoppe-Seyler[8] found that 50 grams of lignin-free filter paper, 25 grams of KOH and 250 cc. of water, heated to 250° C., gave .64 grams of almost pure protocatechuic acid and a trace of catechol.

Practically all the evidence points to the view that lignocellulose, or rather the lignocelluloses, since they vary somewhat among themselves, are chemical combinations of celluloses with other constituents commonly known as lignins. There are, in all probability, several lignins closely related in general structure. Concerning the celluloses, there is a great deal of information available, yet the subject is still one of much theorizing and experimentation.[9] Concerning the lignins, there is as yet very little, if any, really definite information about their structures.

Several theories have been proposed, notably that lignin is a product of the condensation of coniferyl and hydroxyconiferyl alcohols. This theory is generally attributed to Klason.[2] Another theory is that of Cross and Bevan.[10] They are of the opinion that the nucleus of the lignin molecule is a keto — R hexene group,

$$OC \Bigg\langle \begin{array}{c} CH = CH \\ C - C \end{array} \Bigg\rangle CH_2$$
$$(HO)_2 \ (OH)_2$$
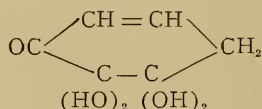
to which are attached other groups, such as methoxyl, acetyl, etc. The form of combination between lignin and cellulose is not definitely known. Most authors[11], [12] assume that it is either an ester or an ether, since cellulose is known to contain alcoholic hydroxyl groups, and lignin is assumed to be either an acid or an alcohol. In addition to these two possible forms, ester and ether, we may include another form, that of an acetal, since the ligneous material present in sulphite waste liquor seems to have several carbonyl groups in the molecule. These proposed forms of combination between cellulose and lignin are in accordance with the characteristic property,[13] that of responding to hydrolytic treatment.

I. Determination of "Free SO₂"

The sum of the sulphurous acid, the bisulphite, and the sulphite present in sulphite waste liquor, all expressed as SO₂, is what is

[8]Hoppe-Seyler. Zeit. Physiol. Chem. 13, 77-82 (1889).
[9]Hibbert, H. J. Ind. Eng. Chem. 13, 256, 334 (1921).
[10]Cross and Bevan. Cellulose, 1918, p. 77.
[11]Schwalbe, C. G. Chemie der Cellulose. Berlin, 1911.
[12]Klein, A. Paper, 24, 351, 409 (1919).
[13]Cross and Bevan. Cellulose, 1918, p. 208.

known as the "free SO_2." It is customarily determined[14] by titration with standard iodine solution, with the ordinary starch solution as indicator. As the end point is a vanishing one, owing to the progressive formation of more SO_2 by the decomposition of the "loosely combined SO_2" (see below), practice is required before results can be duplicated.

It was found that the primary variable factors that must be considered in studying this titration are the dilution and the temperature at which the titration is performed.

A. The Effect of Dilution

To determine the effect of dilution, 10 cc. portions were taken of liquor A.[15] To each a measured amount of distilled water was added. 2 cc. of starch solution (1 :200) were then added and the titration performed in the usual manner. The effect of dilution on the end point varies directly as the dilution, as it represents the amount of standard solution required for the titration of amounts of pure water. The corrections for this effect were determined by running blanks with 10 cc. and 100 cc. of distilled water and drawing a line, give the correction for any dilution. In this way the following data were obtained and the curve plotted. (Table I, Figure I.)

TABLE I.

cc. of H₂O added	Cc. I₂ sol.	Cor.	cc. net	mg. SO₂ per cc. liq.
0	0.6	0.0	0.6	0.07
50	0.7	0.1	0.6	0.07
100	0.9	0.1	0.8	0.09
150	1.0	0.1	0.9	0.10
200	1.0	0.2	0.8	0.09
300	1.3	0.3	1.0	0.11
500	1.6	0.5	1.1	0.12
1000	2.1	0.9	1.2	0.13
Blank	..	..	..	...
10	0.0	..	..	...
1000	0.9	..	..	...

Titrations performed at room temperature, 20° C.
Iodine solution standardized against sodium arsenite.
1 cc. of I₂ solution equivalent to 1.09 mg. of SO₂.

FIG. I
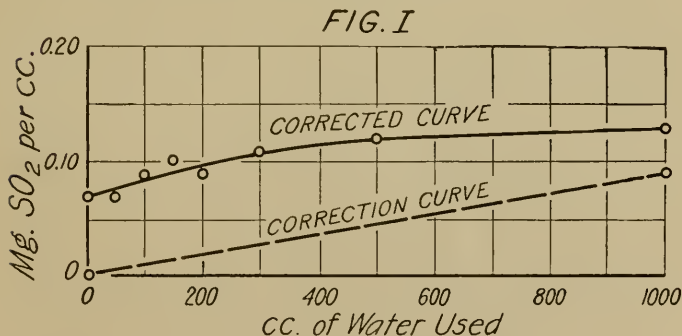
[14]Sutermeister, E. Chemistry of Pulp and Paper Making, 1920, p. 191.
[15]By courtesy of Abitibi Power and Paper Company.

These experiments show that the amount of free SO_2 increases with the dilution at a decreasing rate. This would seem to indicate that there is present some very unstable form on combination of SO_2. However, the small increase in free SO_2 means that it is either present in small amount or that an equilibrium exists between the free and combined SO_2 and that the equilibrium conditions are satisfied by small concentrations of SO_2. When we alter the concentration of the combined SO_2 by diluting, we also alter the concentration of free SO_2 required for the equilibrium. If such an equilibrium exists, the concentrations of SO_2 required are very small.

B. The Effect of Temperature

This effect was determined by taking 10 cc. portions, adding 50 cc. of distilled water and 2 cc. of starch solution, bringing to the required temperature as registered by a thermometer immersed in the liquid by externally heating or cooling the flask and titrating immediately. Temperature has a slight effect upon the end point when distilled water is titrated with iodine solution. To eliminate this effect upon our data, a titration was performed with 50 cc. of distilled water at the highest temperature involved. 0.7 cc. were required. Thus this correction is slight and no appreciable error is introduced if we consider that the correction for the other temperatures is proportional to the temperature. From the data, Table II, a curve, Figure II, was plotted.

TABLE II.

Temp.	Cc. I_2 sol.	Cor.	Net cc. I_2 sol.	mg SO_2 per cc.
1°C	0.7	0.0	0.7	0.08
11°C	0.7	0.1	0.6	0.07
21	0.8	0.2	0.6	0.07
30	0.9	0.3	0.6	0.07
41	1.1	0.4	0.7	0.08
50	1.5	0.5	1.0	0.11
70	3.9	0.7	3.2	0.35
Blank 70	0.7	..	..	...

1 cc. I_2 sol. $=$ 1.09 mg. SO_2.

These results indicate that profound decomposition of SO_2 bearing substance occurs when sulphite waste liquor is heated to even a moderate temperature. Therefore, for strictly concordant results the free SO_2 must be titrated at a low temperature, and preferably at the same temperature every time. This is most easily done by adding ice to the solution. The curve, Figure 1, showing the effect of dilution makes it clear that the error of dilution due to the addition of a small amount of ice is negligible.

II. Determination of "Loosely Combined SO_2."

The sulphur dioxide mentioned above as easily split out of the organic molecule is known as the "loosely combined." It is known by this name because it is readily removable from the organic molecule by treating with alkali solution.

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A. Reaction of Alkali at the Temperature Attained by Use of a Water Bath

One hundred cc. of sulphite waste liquor and one hundred cc. of sodium hydroxide solution (100 g. of NaOH per liter) were mixed

FIG. II

Mg. SO₂ per CC. (y-axis)

Temperature of Titration, °C. (x-axis)
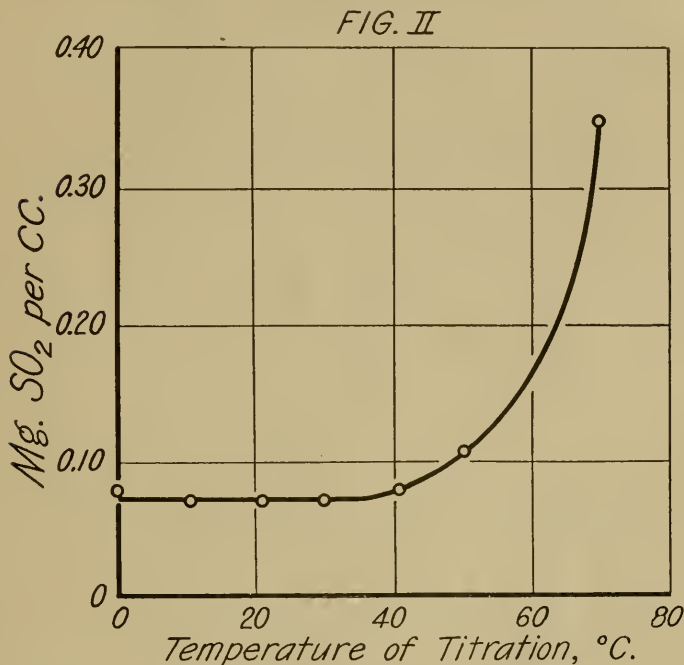
and the flask containing the mixture placed upon a water bath. A thermometer was immersed in the mixture. At intervals twenty-five cc. portions were pipetted out and ice added in sufficient quantity to bring the solution to zero degree centigrade. Sulphuric acid solution (made by diluting acid of specific gravity 1.84 with an equal volume of water) was added, with vigorous agitation until the alkali in the liquor was just neutralized, the amount necessary to neutralize 12.5 cc. of alakli solution having been previously determined. After neutralization, the titration was proceeded with immediately in the usual manner.

In this way, the data given below, Table III, were obtained, and the curve representing them plotted, Figure III. Examination of the curve shows that the mixture of alakli and waste liquor must be allowed to remain on the water bath for at least ten minutes to obtain concordant results, since the amount of SO₂ split out does not become constant before that time has elapsed. Moreover, it is best to leave the mixture on the water bath for the same time interval for each determination.

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B. Reaction at Room Temperature

It was next decided to investigate the reaction at room temperature. Equal volumes of waste liquor and NaOH solution were mixed as before and 25 cc. portions removed and titrated in the

FIG. III
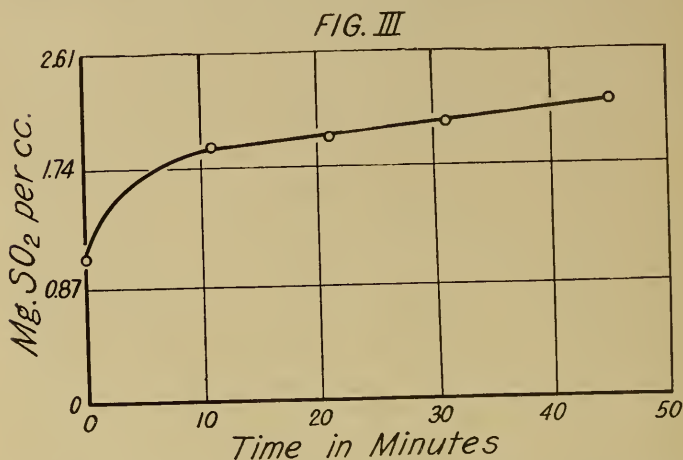
manner described above. Thus we obtain the data of Table IV, shown graphically in Figure IV. Similarly, with liquor B,[16] data for the same kind of a curve were obtained, Table V, Figure 5.

FIG. IV
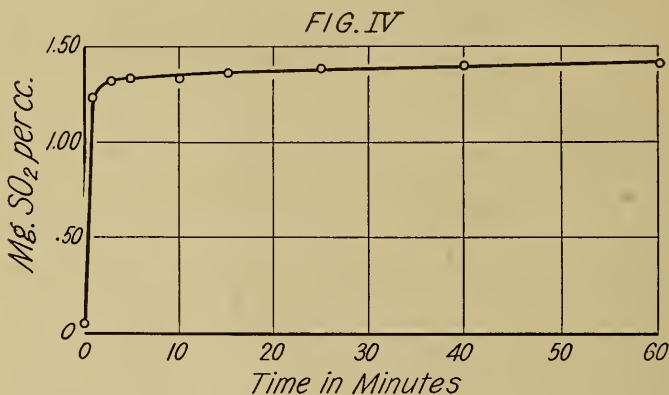
Examination of these curves shows that the reaction is complete or rather comes to final equilibrium in about ten minutes.

If the temperature is raised above room temperature, say, to the temperature attainable by means of a water bath, an additional amount of SO_2 will be split off. If the mixture is cooled to room

[16]By courtesy of Price Bros. & Co.

temperature again, we find that the amount of SO_2 split out is still the same as that split out at the higher temperature. This proves that the increase in amount is not due to a displacement

TABLE III

Time elapsed, min.	Temp. °C	I_2 sol. cc.	mg. SO_2 per cc. liquor
0	44	12.3	1.07
11	88	21.9	1.90
21	89	22.2	1.93
31	89	23.7	2.06
45	88	25.2	2.19
Original liquor, 25 cc.		1.2	0.05

25 cc. of sodium hydroxide solution required 6.5 cc. of H_2SO_4 solution for neutralization with phenolphthalein as indicator. Therefore 3.2 cc. were added each time to neutralize the NaOH before titrating.
1 cc. of standard I_2 solution equivalent to 1.09 mg. of SO_2.

TABLE IV. (Liquor A)

Time elapsed, min.	cc. I_2 sol.	mg. of SO_2 per cc. of liquor
0	...	0.05
1	12.7	1.00
3	15.7	1.24
5	16.1	1.27
10	16.6	1.31
15	16.5	1.30
25	17.3	1.37
40	17.5	1.38
60	17.3	1.37

Room temperature 23° C.
1 cc. of standard I_2 solution equivalent to 0.987 mg. of SO_2.

TABLE V. (Liquor B)

Time elapsed, min.	I_2 sol. cc.	mg. of SO_2 per cc. liquor
0	...	0.02
1	15.6	1.04
3	16.3	1.09
5	16.5	1.10
10	16.1	1.07
15	17.1	1.14
25	17.3	1.15
40	16.9	1.13
60	17.8	1.19
100	18.2	1.21
130	18.3	1.22

Room temperature 23° C.
1 cc. of standard solution of I_2 equivalent to 0.835 mg SO_2.

FIG. V

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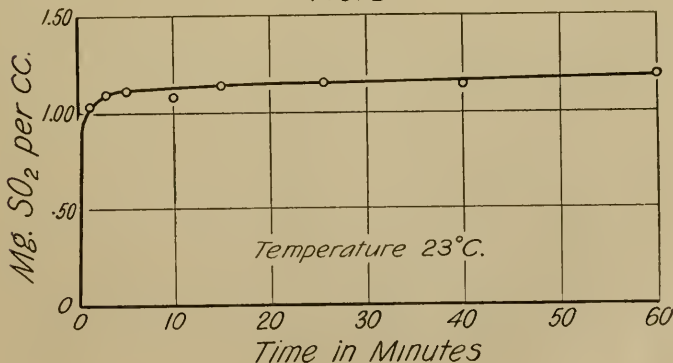
of the equilibrium with the change of temperature. Were the increase in amount of SO_2 split out due to such a temperature displacement of the equilibrium, then reversion to the original temperature should result in a decrease to the amount split out at the original temperature. Therefore, the reaction at the higher temperature must include a different one from that at the lower temperature. Table VI and Figure 6 show the splitting out of additional SO_2 when the temperature is raised.

TABLE VI

Time elapsed, min.	Temp., °C	I_2 sol. cc.	mg. SO_2 per cc. liquor
0	23	. . .	0.05
1	23	12.7	1.00
3	23	15.7	1.24
5	23	16.1	1.27
10	23	16.6	1.31
15	23	16.5	1.30
25	23	17.3	1.37
40	23	17.5	1.38
60	23	17.3	1.37
90	23	17.9	1.41
91	26	17.9	1.41
93	32	17.9	1.41
95	38	17.7	1.40
102.5	53	18.9	1.49
105	58	19.1	1.51
115	74	20.8	1.65
130	85	22.1	1.75
140	87	23.0	1.82
150	89	23.2	1.83
160	89	23.4	1.85
170	89	24.4	1.93

1 cc. of I_2 solution equivalent to 0.986 mg of SO_2.

The examination of the velocities of reaction also shows a difference of reaction under certain conditions. If the same reactions proceed at a higher temperature, then the velocity of reaction is greater at the higher temperature. Assume, for example, that we

FIG. VI
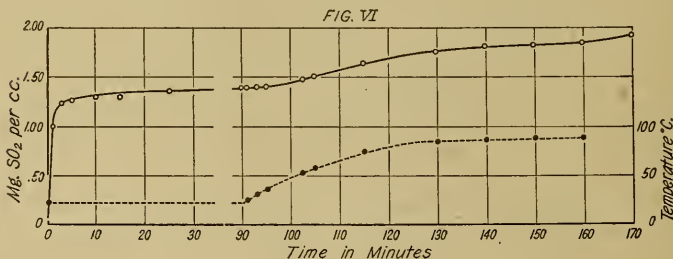
have two reactions taking place at different temperatures. If the velocity of the reaction at the higher is smaller than the velocity of the reaction taking place at the lower temperature, then the reactions are not identical, since for a given reaction an elevation of temperature results in an increase in velocity of reaction.

The ideal way of performing an experiment to determine the velocity of the reaction between sulphite waste liquor and alkali at a temperature higher than room temperature, would be to heat

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up the alkali solution and the waste liquor separately to the desired temperature and then to mix the two. Samples for analysis could be withdrawn from time to time. However, this procedure could not be followed because when waste liquor is heated up separately, a loss of SO_2 occurs.

For this reason the experiment was carried out by heating up the alkali solution and then adding the waste liquor to it. This method had the disadvantage that the temperature is not uniform during the course of the experiment. but rises from the minimum


FIG. VII
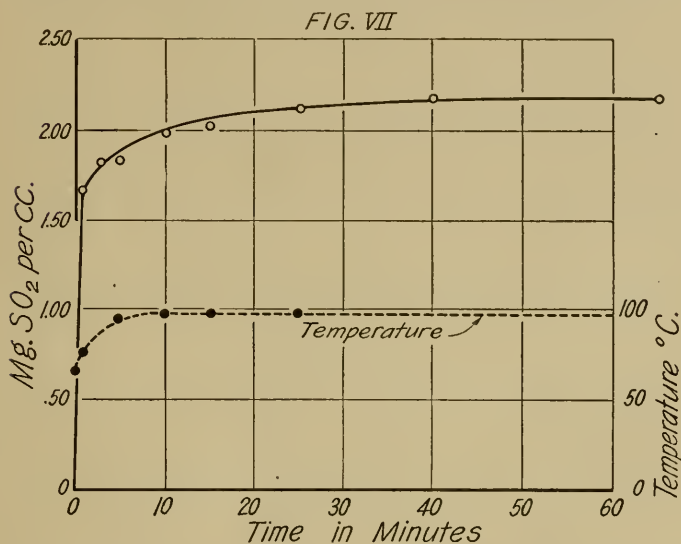
and finally reaches a maximum. However, since at all times the temperature is higher than room temperature, the same data, though not exactly quantitative, would indicate a difference of reaction. Accordingly, the experiment was carried out in this fashion.

The apparatus used consisted of a 500 cc. short-necked round-bottom flask, equipped with a stopper, through which passed a thermometer, reaching almost to the bottom, and a short piece of tubing serving as an air condenser to prevent excessive evaporation. The flask was immersed to about three-quarters of its volume in a boiling water bath. The samples for analysis were withdrawn by temporarily removing the stopper and using a pipette.

The 100 cc. of alkali solution were first placed in the flask and the temperature allowed to reach the desired point. The 100 cc. of sulphite waste liquor were then added and the contents of the flask thoroughly mixed. The temperature was noted then and at the time of the removal of each sample. The initial time was taken at the instant when the addition of the waste liquor was completed.

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In these experiments the molecular ratio of NaOH to SO₂ split out is about 80 to one. In other words, the NaOH is present in so large an excess that its concentration does not alter appreciably during the course of the reaction and therefore we may neglect the changes in concentration of NaOH in our discussion.

FIG. VIII
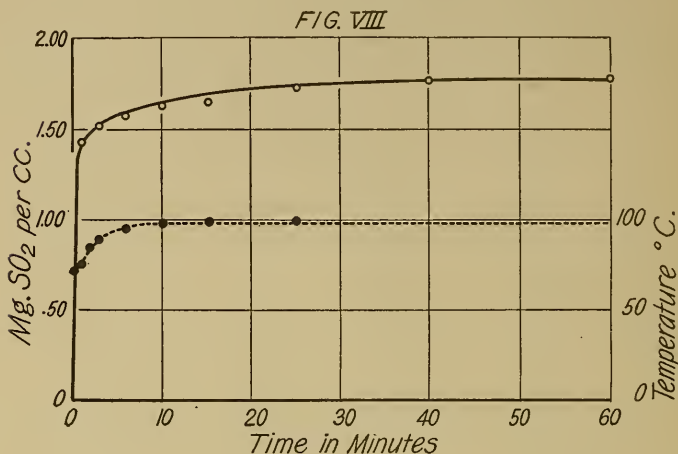
In the manner described above, data were obtained for the reactions at the higher temperature of the two liquors previously investigated. These data are shown in Tables VII and VIII, and graphically in the corresponding curves.

TABLE VII (liquor A)

Time elapsed min.	Temp. ° C	I₂ sol. cc.	mg. SO₂ per cc. liquor
0	65	....	0.05
1	74	19.7	1.65
3	87	21.6	1.81
5	94	21.7	1.82
10	97	23.5	1.97
15	97	24.1	2.02
25	97	25.2	2.11
40	97	25.9	2.17
65	97	25.8	2.16
90	97	26.3	2.20
Allowed to cool to 23		25.8	2.16

1 cc. of standard I₂ solution equivalent to 1.047 mg. of SO₂.

TABLE VIII (liquor B)

Time elapsed min.	Temp. ° C	I₂ sol. cc.	mg. SO₂ per cc. liquor
0	69	....	0.02
1	73	.21.4	1.43
3	88	22.7	1.51
6	94	23.4	1.56
10	97	24.3	1.62
15	97	24.6	1.64
25	99	25.7	1.71
40	98	26.5	1.76
60	98	26.6	1.77
90	98	27.4	1.82
Cooled to 23		27.0	1.82

1 cc. of standard I₂ solution equivalent to 0.835 mg. of SO₂.

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Let us examine these curves. At the low temperature, the reaction is completed in approximately ten minutes. At the high temperature, the reaction cannot be considered complete until about forty minutes have elapsed. In other words, the net reaction at the higher temperature is slower than that at the low. This proves that there must be another reaction taking place at the higher temperature. This reaction proceeds so slowly that the net velocity, involving the low temperature reaction speeded up by the elevation of the temperature, is less than the velocity of the low temperature reaction.

In addition to the discussion of the data on the velocities of the reactions at the different temperatures, we have available other data supporting our conclusion, i. e., the data on the actual amounts of SO_2 split out. For example, with liquor A the amount of SO_2 split out at room temperature was 1.38 mg. per cc. The amount split out at the higher temperature was 2.16. One and one-half times 1.38 is 2.07. In other words, it looks as if for every two moles of SO_2 split out at the low temperature, there is an additional mole which can be removed at the higher temperature. The same ratio is true for liquor B. The figures for this liquor are 1.22 at the low temperature and 1.80 at the high. One and one-half times 1.22 is 1.83. Tabulating these figures for convenience in examining them we have:

Liquor	Split out at Low temp. L.	Split out at High temp. H	Ratio L:H
A	1.38	2.16	2:3.13
B	1.22	1.80	2:2.95

Considering the error in titrating and the probable presence of many compounds in small amounts, the agreement of the figures is quite good.

We have additional evidence of the presence of these two kinds of SO_2 in combination. When sulphite waste liquor is boiled, there occurs an escape of SO_2 from the liquor. For example, in a modification of one of the industrial processes for the production of alcohol by the fermentation of sulphite liquor, one step consists in boiling the liquor to lower its SO_2 content. This is assisted by the passage of air through the liquor to carry off the SO_2. Since the waste liquor is acid, this may be considered to be the effect of acid

TABLE IX

Time elapsed hrs.:min.	I_2 sol. cc.	mg. SO_2 per cc. liquor	
0:00	17.7	2.42	
1:25	16.9	2.32	boiling commenced
2:00	13.8	1.89	
2:36	12.9	1.77	
3:14	12.2	1.67	
4:10	11.8	1.62	
5:16	11.9	1.63	
6:10	11.5	1.58	
6:38	11.8	1.62	
7·15	11.5	1.58	

1 cc. of standard I_2 solution equivalent to 1.37 mg. of SO_2.

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treatment. After several hours of boiling, the SO_2 content reaches a nearly constant figure.

We have performed the experiment in the laboratory and have examined the SO_2 content during the course of boiling. Some of the data are here reproduced, together with their graph, Table IX, Figure 9.

In the analyses, the SO_2 was split out by alkali at a high temperature, that attainable by a water bath. These data lead to the same conclusion as the data on the velocity of reaction, namely, that there are two kinds of SO_2 and that one kind is present in an

FIG. IX
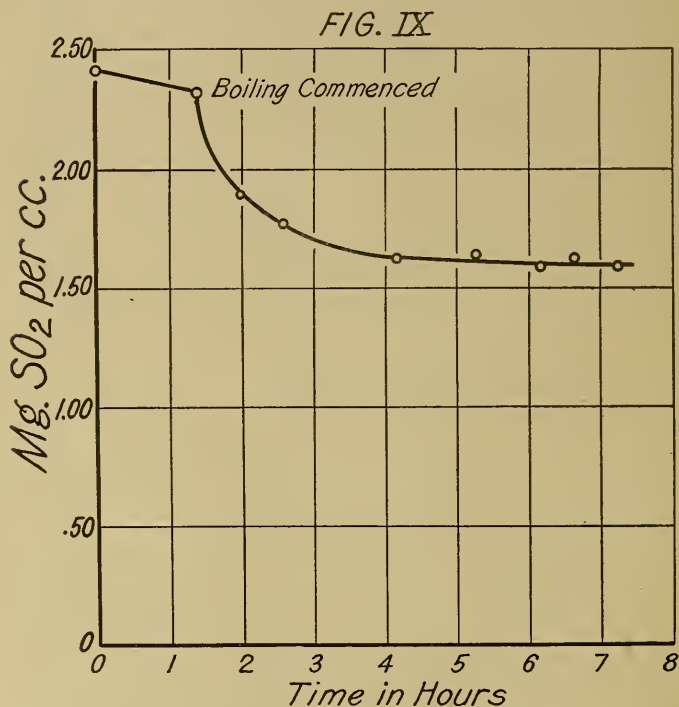
amount twice that of the other. For example, one liquor showed 2.42 mg. of SO_2 per cc. before heating was commenced, and after about four hours, when the SO_2 content had reached a minimum, or rather a nearly constant figure, 1.62 mg. per cc. The amount removed by boiling was 0.80 mg. per cc., while the amount unaffected was 1.62. One is approximately twice the other.

The total amount of sulphur is the liquor, expressed as milligrams of SO_2 per cc. is about 7 in the case of liquor A. Therefore, in addition to the two kinds of SO_2 already discussed, there must be at least one more kind, and there probably are several. These, however, are not removed by alkali treatment nor by boiling.

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Summarizing:

1. The titrations for free SO_2 and loosely combined SO_2 have been investigated, and the conditions laid down for the most accurate titrations.

2. The splitting out of SO_2 by means of alkali has been investigated, and it has been found that there are two kinds of SO_2 split out. One is split out at room temperature and the other only when the temperature is elevated.

3. The removal of SO_2 from sulphite waste liquor by boiling has been investigated and it has been found that after about four hours the SO_2 content reaches a nearly constant figure. Of the loosely combined, one part is removed by boiling while two parts remain unaffected.

Lignin Sulphonic Acids

The technology of the sulphite pulp process is quite involved. The yield and the character of the pulp varies with the cooking liquor and with the manner in which the cook is carried out. Chemically, the process consists of the digestion of the wood in calcium bisulphite solution containing an excess of sulphurous acid. The digestion takes place under pressure and lasts about 10 hours.[1] The net result of this operation is the conversion into soluble materials of all the non-cellulose constituents of the wood. Some of these constituents dissolve without reaction, others merely undergo hydrolysis, while the balance react with the bisulphite and sulphurous acid in the liquor.

In this investigation we have been concerned with the nature of the substances which have reacted with bisulphite and sulphurous acid. Our primary purpose was to ascertain whether there is but one, or several such substances. Our results led to the conclusion that there is a number of such substances.

A large number of woods are characterized by constituents of an adventitious or transient nature, such as the tannins, gums, essential oils, alkaloids, etc. In some cases these have been thoroughly investigated and a few are widely used in industry and in the arts. But comparatively little is definitely known of the fundamental tissues which we may speak of as the wood-substances. There have been many attempts to resolve these wood-substances into proximate constituents but so far these attempts have met with but little success. The problem is fraught with many difficulties and though it has been attacked by many investigators[2] the results are as yet inconclusive. So far as they lend themselves to interpretation they would seem to indicate that there is some degree of uniformity in composition despite the structural disparity and the widely varying character of the substances found in the woods of different species.

The gradation from the cotton cellulose, through the different kinds of cellulose, on through the so-called lignin or non-cellulose, is really so gradual that it is not possible to make a sharp line of demarcation. The celluloses obtained from woods, being products of the resolution and decomposition of the wood, vary both in character and proportion with the treatment by which they are prepared.

1. A typical cook would be approximately for ten hours at 140°C. with a pressure of about 90 lbs. At the start of the cook the liquor would contain about 4.4% total sulphur dioxide of which 1.3% would be combined as calcium bisulphite.

2. The chemical literature in general and the literature on cellulose abounds with references on this subject.

Closely related to cotton cellulose, which is usually taken as the standard type of cellulose, are the celluloses of flax, hemp, china grass and others. These are obtained from the plants in question by some purifying process. They present slight differences from cotton cellulose in external physical characteristics and chemical properties. This indicates slight differences in chemical constitution.

Next we have the celluloses which are characterized by a higher percentage of oxygen, the presence of active carbonyl groups and sometimes the presence of methoxyl groups. These are further characterized by the splitting off of furfural on treatment with hydrochloric acid. They may be termed natural oxycelluloses.

We have still a further group, that of the hemicelluloses, closely resembling the true celluloses but easily hydrolyzed into simple carbohydrates by the action of dilute acids or alkalies. Then we have the carbohydrates known as the lignins which represent still further variation of cellulose structure.

In brief, we have in wood tissues combinations of these substances and of the celluloses making up the fibers. These are termed "lignocelluloses."
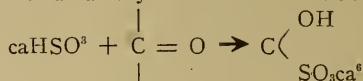
Most authors[3] assume that the form of combination existing between cellulose and lignin (terms which we use in the generic sense) is either (a) that of an ether, or (b) an ester, or a form involving both. In support of (a) it may be said that the ligneous material in sulphite waste liquor has alcoholic hydroxyl groups. Cellulose is known to contain alcoholic hydroxyl groups. It is the union of these groups that gives the ether linkage. For (b) it is necessary to assume that lignin is an acid. Evidence of this acidic character is given by the solubility of lignin in alkalies and by the acid character of groups, such as acetyl, that may be split off from it.[4] In addition to these two linkages, we may add the possibility of an acetal, since the waste liquor shows certain aldehyde reactions, e. g., with phenylhydrazine. All these forms of combination between lignin and cellulose are in accordance with the characteristic property of the lignocelluloses, that of responding to hydrolytic treatment.[4]

We may regard the reactions in the digester as made up of a hydrolysis, followed, or rather accompanied, by the interaction of the non-cellulose products of the hydrolysis with the chemicals of the cooking liquor. In this way the reverse reaction, that of condensation, is prevented, the hydrolysis promoted, and the undesirable substances made soluble.
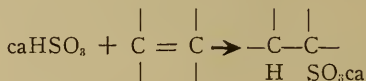
In the sulphite process, consideration of the possible reactions that may take place reveals that there may be any or several of the following:[5]

3.   Schwalbe, C. G. ....Die Chemie der Cellulose.   1911.
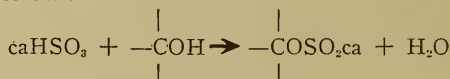4.   Cross and Bevan. ......Cellulose.   1918.
5.   Schwalbe, C. G. Loc. cit.

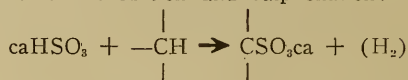(1) The formation of an aldehyde or ketone addition product:

$$caHSO_3 + \overset{|}{\underset{|}{C}} = O \rightarrow C\begin{cases} OH \\ SO_3ca^6 \end{cases}$$

(2) The saturation of a double bond:

$$caHSO_3 + \overset{|}{\underset{|}{C}} = \overset{|}{\underset{|}{C}} \rightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{SO_3ca}{C}}-$$

(3) Esterification:

$$caHSO_3 + -\overset{|}{\underset{|}{C}}OH \rightarrow -\overset{|}{\underset{|}{C}}OSO_2ca + H_2O$$

(4) Simultaneous oxidation and sulphonation:

$$caHSO_3 + -\overset{|}{\underset{|}{C}}H \rightarrow \overset{|}{\underset{|}{C}}SO_3ca + (H_2)$$

In all cases where a separation is effected between the cellulose and the non-cellulose, it is unsafe to assume that the bond between the two classes of materials is merely broken. There probably always occurs some alteration of one, and more likely both, of the substances dissolved and the substances remaining insoluble in the reagent. Of the two major constituent groups, the celluloses have been much investigated because of their many uses. The lignin compounds have had no uses and accordingly have been more or less neglected.

The sulphite waste liquor remaining after the digestion of the wood and the removal of the cellulose varies in color from a light yellow to a dark brown, is slightly acid and smells slightly of SO_2. It has a specific gravity of about 1.05 and contains about 10 per cent of solids. It is strongly reducing to Fehling's solution and reacts with phenylhydrazine to give a copious tarry mass.

Lindsey and Tollens[7] found that after removal of sulphuric acid from the sulphite waste liquor by means of barium hydroxide, they could obtain a heavy precipitate with lead acetate. It had a composition, the organic portion of which was expressed as $C_{28}H_{30}O_{12}$. They also obtained a precipitate with hydrochloric acid and assigned the formula $C_{26}H_{30}SO_{10}$ to it. A brominated derivative was also prepared to which they assigned the formula $C_{26}H_{28}Br_4SO_{11}$. They concluded that the major part of the dissolved organic substances behaves as a homogeneous complex as they were unable to resolve it into its proximate constituents.

Seidel and Hanak[8] after removal of sulphuric acid precipitated certain material by adding alcohol. The percentage of CaO was determined and a part of the precipitate then converted into

6. ca = $\frac{1}{2}$ Ca.
7. Lindsey and Tollens...Ann. 267, 341 (1892). J. Soc. Chem. Ind. 11, 835 (1892), 12 287 (1893) Z. angew. Chem. 5 154 (1892).
8. Seiden and Hanak.....J. Soc. Chem. Ind. 17 596, 863 (1898).

the barium and a part into the zinc salt. The authors found that the ratio of the metals combined in the salts was practically the same as that of their atomic weights. From this they concluded that the precipitate obtained was a salt of a definite organic acid which is the principal constituent of the organic matter in the waste liquor.

Krause[9] obtained a chlorine derivative by adding bleaching powder to the liquor. This derivative, after purification with alcohol and ether, showed on analysis a composition corresponding to the formula $C_{25} H_{29} ClSO_{32}$.

Klason[10] separated "calcium lignosulphonate" by adding crystallized calcium chloride as long as any went into solution. He obtained a heavy precipitate which was filtered and washed with alcohol. This salt was decomposed by adding sulphuric acid to its solution in just sufficient quantity to react with all the lime present. The calcium sulphate formed was filtered off and the solution concentrated. Alcohol was then added to complete the precipitation of the calcium sulphate. The alcohol was evaporated from the filtrate, the solution diluted and neutralized with barium hydroxide. Any barium sulphate found was allowed to settle out. The addition of alcohol then precipitated the so-called barium lignosulphonate. Analysis of this salt pointed to the formula $C_{40} H_{41} O_{17} S_2 Ba$. Molecular weight determinations gave results in the neighborhood of 6,000. Accordingly Klason assigns the formula $(C_{40} H_{42} O_{11})_6$ to the lignin. To the $C_{40} H_{42} O_{11}$ Klason assigns 3.7 methoxyl groups and 1.1 hydroxyl groups. Of this work it may be said that there is nothing involved in the method that would allow us to consider this material a compound. In fact the analytical data immediately indicate that it must be a mixture. Hence it is a little far fetched to make deductions concerning lignin with this as a basis.

Klason[11] later discovered that there was a "calcium lignosulphonate" which was not precipitated upon the addition of calcium chloride but which remained in solution. It could be precipitated by means of naphthylamine hydrochloride. This latter he terms a β lignin derivative. That precipitable by calcium chloride he called an α lignin derivative.

Hönig and Spitzer[12] attempted to separate the material of the liquor by fractional precipitation with alcohol but all their fractions with one exception, calculated as salts of lignosulphonic acid, showed sensibly the same composition.[13] Melander[14] found that the product salted out of waste liquor with sodium chloride

9. Krause, H............J. Soc. Chem. Ind. 25 493 (1906).
10. Klason, P............Beitrage zur Kenntniss der Chemischen Zusammensetzung der Fichtenholzes. 1911.
11. Klason, P............Chem. Zentr. 90 92 (1919). J. Soc. Chem. Ind. 38 570A (1919).
12. Hönig, M............Monatsh. 39 871 (1918).
13. Klason, P............Ber. 53B 1864 (1920).
14. Melander, K. H. A....Cellulosechem. 2 41, 69, (1921), Paper 28 No. 21 p. 19 (1921). J. Soc. Chem. Ind. 40. 620A (1921). Chem. Soc. Abs. 116Pt, (1919).

differed from the product obtained by Klason with calcium chloride.

The precipitation schemes given above are in agreement with the customary schemes for the precipitation of an emulsoid colloid by the use of a strong electrolyte or by the addition of alcohol. Where we have present a mixture of substances in the colloidal state, in general such methods would result in the precipitation of mixtures.

By precipitating, dissolving and reprecipitating, Hofmeister[15] succeeded in obtaining pure albumen (*i. e.,* crystallized) from colloidal albumen. Von Weimarn,[16] adopting the same principle, prepared crystalline gelatine and agar, typical colloids. We have adopted a similar procedure to separate the material precipitated with calcium chloride, with the idea of studying its purity. We have fractionally precipitated and then refractionated after dissolving. These experiments were as follows:

Three liters of liquors[17] were evaporated to about 800cc. and the calcium sulphate filtered off. The resultant solution was placed in a beaker and stirred mechanically. Calcium hydroxide suspension was added until the solution was neutral to litmus paper. Crystallized calcium chloride was then added in 50 g portions until a precipitate appeared, and the solution heated on the water bath for about two hours, *i. e.,* until the precipitate coagulated. Thereupon it was filtered off with suction, sucked as dry as possible, and weighed. In all cases the procedure was exactly the same, so that the percentage of moisture in the precipitate was the same. An additional 50 g of calcium chloride were added to the filtrate and the precipitate so obtained treated in the same manner as the preceding one. The addition of calcium chloride was continued until no further precipitation took place. In this way, a fractionation of the calcium chloride precipitate was effected and the data given in Table I obtained and curve in the figure drawn. The wide range during which precipitation takes place, 150 g to 400 g of calcium chloride, would seem to indicate that there is a mixture being precipitated.

Table I

Total g CaCl$_2$ added	Ppt.	Ppt.	Grams total Ppt.
50	None	0	0
100	None	0	0
150	None	0	0
200	A	95	95
250	B	85	180
300	C	80	260
350	D	45	305
400	E	15	320
450	..	0	320

The precipitates A, B, C, D, and E were dissolved in proportionate amounts of water, 2 cc. per gram. The appearances of the

15. Hofmeister, F.........Z. physiol. Chem. 14, 165 (1889), 16—187
          1892).
16. Von Weimarn, P. P...Grundzüge d. Dispersoid Chemie. 1911.
17. By courtesy of the Hammermill Paper Co.

different solutions were quite distinctive: A, muddy; B, black; C, dark wine color; D and E, a lighter brown. These solutions were treated in a manner similar to the original evaporated liquor in an attempt to accomplish a still further separation of the compounds. The data are shown in the Tables II, III, IV, from which precipitation curves similar to that in the figure can be drawn.

Table II

Total g CaCl$_2$ added	Ppt.	Grams Ppt.	Grams total Ppt.
0	. .	0	0
25	A$_1$	25	25
50	A$_2$	17	42
75	A$_3$	7	49
100	. .	0	49

Table III

Total g CaCl$_2$ added	Ppt.	Grams Ppt.	Grams total Ppt.
0	. .	0	0
10	. .	0	0
20	. .	0	0
30	. .	0	0
40	B$_1$	40	40
50	B$_2$	10	50
60	B$_3$	6	56
70	. .	0	56

Table IV

Total g CaCl$_2$ added	Ppt.	Grams Ppt.	Grams total Ppt.
0	. .	0	0
10	. .	0	0
20	C$_1$	14	14
30	C$_2$	10	24
40	C$_3$	4	28
50	. .	0	28

A$_1$, B$_1$, C$_1$, D and E (D and E were not fractionated because of the small quantity) were then converted to the barium salt by the method described by Klason. The method used for the several fractions was the same. In every case the final precipitation was accomplished by pouring the aqueous solution into twice its volume of 95 per cent alcohol. The precipitates were sucked dry, washed with 95 per cent alcohol, and dried for several days over concentrated sulphuric acid.

These barium salts were then analyzed by organic combustion[18] to determine the percentage of carbon and hydrogen. The sample subjected to combustion was contained in a platinum boat. To provide against any sulphur that might be burned off, a plug of lead peroxide-minimum mixture was inserted in the combustion tube in the manner usual for such compounds. The percentage of ash was determined by weighing the residue from the combustion. The analytical data are given in Table V.

18.   Fisher, H. L..........Laboratory Manual of Organic Chemistry, 1920.

Table V

	Wt. of sample	Wt. of ash	H_2O found	CO_2 found	% Ash	% C	% H
A_1	.2116	.1136	.0547	.2132	53.69	27.48	2.89
B_1	.2035	.0398	.0848	.3559	19.56	47.69	4.66
	.2181	.0431	.0936	.3858	19.75	48.24	4.80
				Av.	19.66	47.97	4.73
C_1	.2368	....	.1016	.3975	....	45.67	4.80
	.2121	.0453	.0849	.3531	21.36	45.40	4.48
				Av.	21.36	45.54	4.64
D	.2257	....	.0950	.3358	....	40.55	4.41
	.2220	.0592	.0915	.3278	26.66	40.26	4.61
				Av.	26.66	40.41	4.51
E	.2028	.0510	.0824	.3184	25.14	42.82	4.54
	.2029	.0524	.0790	3189	25.82	42.88	4.36
				Av.	25.48	42.85	4.45

Because of the likelihood of there being extraneous mineral matter such as barium chloride, etc., contaminating the barium salts, the analyses were calculated to the ash-free basis. The results are given in the following table. (Table Va).

Table Va

	% Ash	% Combustible	% C	% H	Ash-free Basis		
					% C	% H	Ratio C/H
A_1	53.69	46.31	27.48	2.89	59.4	6.2	9.7
B_1	19.66	80.34	47.97	4.73	59.7	5.9	10.1
C_1	21.36	78.64	45.54	4.64	57.9	5.9	9.8
D	26.66	73.34	40.41	4.66	55.1	6.4	8.6
E	25.48	74.52	42.85	4.45	57.6	6.0	9.6
Cellulose					44.2	6.3	7.0

We can now plot a curve showing the composition of the material fractionated by the calcium chloride precipitation. For example, A_1 is the material which comes down when precipitation starts, B_1 the material precipitated when 200 grams of calcium chloride have been added, and so on. This curve is plotted on the same sheet as the one showing the course of the precipitation, with the grams of calcium chloride as absiccæ.

After sufficient calcium chloride has been added to start precipitation, there occurs a steady precipitation of lignin mixtures for the range that the precipitation curve is a straight line. When the lignins have all been precipitated, or nearly so, the most difficultly precipitable material comes down. This stage is represented by the section of the curve from D to E. During this interval the curve of precipitation is not a straight line, but indicates from its shape that the substances coming down are not as readily precipitated as those preceding it, and consequently might be expected to differ from them in composition.

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The elementary analyses show percentages of carbon varying from 59.7 to 55.1, percentages of hydrogen varying from 6.4 to 5.9. The ratio of percentage of carbon to that of hydrogen varies from 8.6 to 10.1. This ratio for cellulose is 7.0. In other words, the ratio of carbon to hydrogen is higher in lignin than in cellulose.
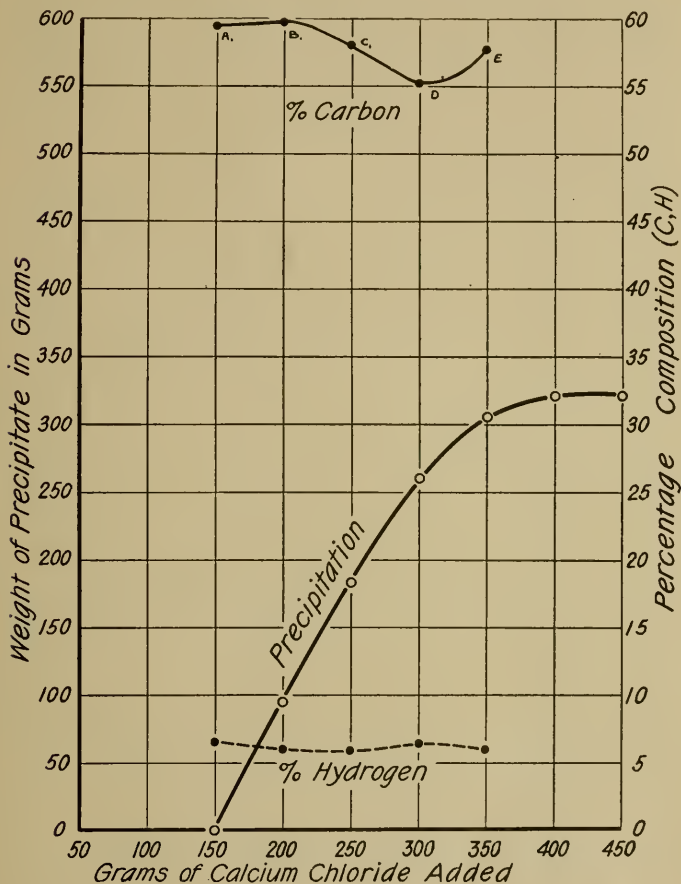
The above all leads to the interesting conclusion that the barium salt accepted by Klason and others as a more or less single definite compound is not by any means a single substance, but on the contrary, contains several substances of varying composition. This mixture accounts for the strange values Klason obtained for the hydroxyl number, etc., of his salts and for the discrepancies that have been found by various workers.[19]

19. Loc. cit. 7, 8, 9, 12, 14.

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Sulphite Waste Liquor as a Fuel

In the manufacture of alcohol[1] from sulphite waste liquor it is of advantage to concentrate the liquor to about 20% solids to reduce the size of the installation required for fermentation and distillation. In conjunction with the alcohol process, the liquor might be further evaporated and utilized as a liquid fuel. It could be burned as a pitch containing 50 per cent solids by spraying through a burner in a way similar to that in which the waste liquors of the sulphate process are burned in one recovery process[2]. This would be an addition to the power plant of the pulp mill.

When the sulphite liquor obtained after the removal of the alcohol by distillation is evaporated, there remains a residue showing, on the dry basis for a typical liquor, a heat value of 7950 B. t. u. per pound with an ash content of about 13.9 per cent. For each ton of pulp there is obtained about 1,100 gallons of liquor after the removal of the alcohol. This weighs 9,900 pounds and contains 14 per cent of solids, i. e., 1,386 pounds. To concentrate this to 50 per cent solids requires the removal of 7,128 pounds of water with the formation of a mobile pitch containing 50 per cent solids and weighing 2,772 pounds.

Heat value of the pitch containing one pound of solid:

B. t. u. developed by burning the solid	7,950
B. t. u. required	
to heat the water from 120° to 212° F........ 92	
to evaporate the water 970	
to heat this vapor to flue temperature estimated as 500° F. .47 (500-212)................135	
B. t. u. unavailable because of presence of water........	1,197
	———
B. t. u. available	6,753

If this pitch is burned under a boiler to give steam at 150 pounds pressure, there will be obtained an efficiency of say 60 per cent. Then there will be obtained from feed water at 120° F:

$$\frac{6,753 \times .60}{1,107} = 3.66 \text{ pounds of steam at 150 pounds.}$$

1,107 is the number of B. t. u. required to convert 1 pound of water at 120° F. to one pound of steam at 150 pounds gauge pressure. The steam generated can be used for the development of power in non-condensing steam engines. The exhaust of such engines can be used to avaporate the liquor in multiple effect evaporators. On the basis of this system these calculations follow:

A simple non-condensing steam engine, using steam at 150 pounds

1. McKee, R. H.   U. S. Pat. No. 1,273,392, July 23, 1918.
          Paper, *24*, 584 (1919).
          Pulp Paper Mag., Canada 18, 715 (1920).
2. Moore, H. K,   Trans. Amer. I. Chem. Eng., *10*, 177 (1917).
          Paper *25*, 1157, 1197, 1241 (1920).

pressure, has a steam consumption of about 30 pounds per indicated horsepower hour. Therefore from the steam there can be obtained

$$\frac{3.66}{30} = .122 \text{ I. H. P. per pound of residue.}$$

The exhaust steam from this type of engine is at a pressure of three to five pounds and is about 88 per cent dry. Assuming that owing to pipe condensation and other heat losses it delivers but 75 per cent of the theory to the evaporators, there are delivered to the evaporators

$$.88 \times .75 \times 3.66 = 2.42 \text{ pounds of low pressure steam per pound of residue.}$$

In a plant producing one hundred tons of pulp per day, there can be obtained

$$100 \times 1,386 \times \frac{.122}{24} = 703 \text{ I. H. P. per 24 hour day}$$

$$100 \times 1,386 \times 2.42 = 335,000 \text{ pounds of low pressure steam}$$

To evaporate the 1,100 gallons to 50 per cent solids as calculated above requires the removal of 7,128 pounds of water. A triple effect evaporator of the ordinary type requires about .372 pounds of low pressure steam per pound of water evaporated and therefore can evaporate 7,128 pounds of water if furnished with 2,650 pounds of steam. For a hundred ton plant this amounts to 265,000 pounds. Therefore we have an excess of steam above the requirements for the evaporation of the liquor to the state of 50 per cent solids. This amounts to 335,000 less 265,000 or 70,000 pounds of low pressure steam per hundred tons of pulp.

In other words, for a plant producing one hundred tons of pulp per day, the fuel available will give, in addition to the energy required for the evaporation of the discharge from the alcohol still to a concentration adapted for burning, 703 I. H. P. for 24 hours and 70,000 pounds of low pressure steam.

Although such an installation has the important advantage of disposing of the waste liquor nuisance, it might be argued that it would prove a financial burden to the pulp mill because of the operating charges. The following approximate tabulation of costs and credits shows that such an argument is groundless.

Triple-effect evaporator to evaporate 30,000 pounds of water
per hour $75,000
Boiler 1,000 H. P. installed 40,000
Engines, 700 H. P. installed 14,000
                                                        ─────────
                                                         $129,000
20 per cent interest, depreciation, repairs, etc.............. 25,800
Labor, 2 x 24 x 50 x 300 7,200
                                                        ─────────
                                                          $33,000

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With the horsepower year at $190 and coal at $6, the yearly credit value would be:

For 703 H. P. 63,300

For 70,000 pounds of steam per day at 10 pounds per pound of coal for 300 days 6,300

Total yearly credit value $69,600
Cost of operation 33,000

Net yearly credit value $36,600

CONCLUSIONS

In this investigation the following were accomplished:

(1) It was discovered that the loosely combined sulphur dioxide is present in sulphite waste liquor in two distinct forms of combination. This is a contribution to the knowledge of the chemistry of the sulphite process as well as to the knowledge of the composition of the waste liquor.

(2) A method has been devised for effecting at least a partial separation of the lignin compounds. This is an important advance in the study of their structure.

(3) A method has been proposed, which in conjunction with the manufacture of alcohol, utilizes a part of the material, disposes of the remainder, and eliminates the nuisance, at a profit.

VITA

George Barsky was born August 26, 1896, in the City of New York. He received his elementary education in the New York City Public Schools from which he graduated in 1910. He graduated from Townsend Harris Hall in 1913 and entered Columbia College, from which he received the B. S. degree in 1916. He entered the Engineering School in 1916 and was awarded the degree of Chemical Engineer in October, 1918. During the year 1917-1918 he held the position of Research Assistant in the Department of Chemistry, Columbia University. On October 1, 1918, he was called into active service in the U. S. Army, of which he had been a member in reserve. Upon his honorable discharge in January, 1919, he was employed by Professor Ralph H. McKee as a research assistant.
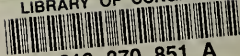
From July, 1919, to July, 1921 he held the Samuel Willard Bridgham Fellowship. Under the grant of this fellowship, the foregoing investigation was pursued. In October, 1921, he received the degree of M. A. from Columbia University.

He is the author of the following articles:

Fuel Value of Volatile Liquid Mixtures, J. Ind. Eng. Chem. *12*, 77 (1920).

Fuel From Sulphite Waste Liquor (with Ralph H. McKee), Paper *26*, 368 (1920).